

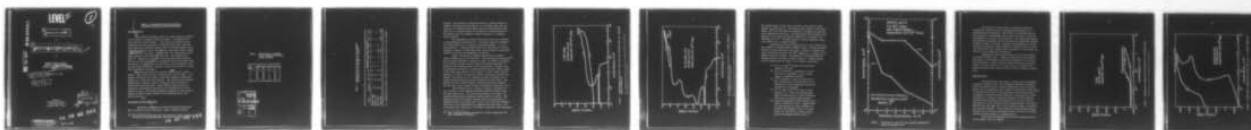
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BATTELLE COLUMBUS LABS OHIO
INVESTIGATING LOCALIZED CORROSION AND SPUTTERING FEASIBILITY OF--ETC(U)
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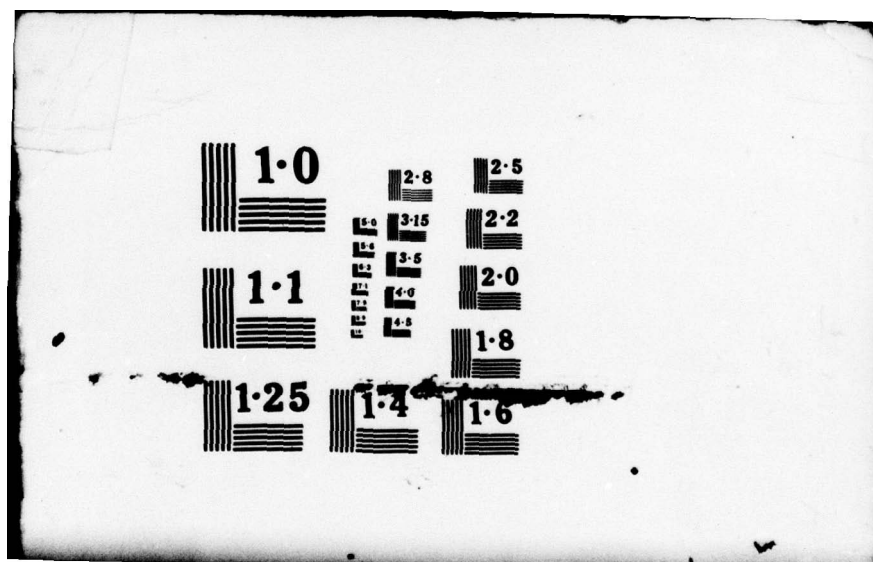
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⑨ SEMIANNUAL STATUS REPORT.

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⑥ INVESTIGATING LOCALIZED CORROSION AND SPUTTERING
FEASIBILITY OF AMORPHOUS CHROMIUM-CONTAINING ALLOYS.

See 19053581

to

OFFICE OF NAVAL RESEARCH
MATERIAL SCIENCES DIVISION
(Contract No. N00014-77-C-0488)

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⑪ 25 Oct 77 October 25, 1977

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Phase I. Determining the Role of Initiation Processes on the Rate of Localized Corrosion

Alloy Preparation

Five different amorphous alloys have been prepared at Battelle for the purpose of studying localized corrosion. The compositions of these alloys are shown in Table 1. The alloys were prepared by first vacuum melting proper quantities of appropriate high purity components and casting into conventional ingots. Next, thirty gram charges of each ingot were separately cast by melt spinning into amorphous metal ribbons, 31 ^{micrometer} ~~um~~ thick and 0.76 mm wide. They were spun onto a water-cooled copper wheel rotating at about 2550 m/sec (5000 fpm). The atmosphere was argon.⁽¹⁾ Although the structures of the individual ribbon specimens have not yet been characterized by transmission electron microscopy (TEM), the presence of limited ductility and extreme corrosion resistance indicate that they are amorphous. TEM may be used at a later date to provide detailed structural information.

Several other alloys are included in ~~our~~^{THE} study for various reasons. These alloys and their compositions are shown in Table 2. The Metglas compositions were chosen to incorporate amorphous compositions prepared by a source other than Battelle. T304 stainless steel is being used because it exhibits classical pitting and crevice corrosion in halide-containing electrolytes. Incoloy 800 was selected because it represents a conventional crystalline alloy of similar Fe, Ni, and Cr content as Alloy 5, and thereby furnishes an indication of the corrosion behavior provided by these elements in the crystalline rather than amorphous state.

Preliminary Corrosion Evaluation

Preliminary investigation is being performed with bulk specimens in simulated crevice electrolytes, namely, acidified chloride

(1) Melt spinning was performed under the direction of Robert Maringer of Battelle's Materials Resources and Process Metallurgy Section.

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TABLE 1. COMPOSITIONS OF AMORPHOUS
ALLOYS PREPARED AT BATTELLE
BY MELT SPINNING

| Alloy Number | Composition, atomic percent | | | | |
|-----------------|-----------------------------|----|----|----|---|
| | Fe | Ni | Cr | P | B |
| 1 | 50 | 30 | 0 | 14 | 6 |
| 2 | 47 | 30 | 3 | 14 | 6 |
| 3 | 45 | 30 | 5 | 14 | 6 |
| 4 | 42 | 30 | 8 | 14 | 6 |
| 5 | 36 | 30 | 14 | 14 | 6 |

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TABLE 2. COMPOSITIONS OF ALLOYS USED IN THE CORROSION
EVALUATION AND NOT PREPARED AT BATTELLE

| Alloy | Amorphous | Composition, atomic percent (a) | | | | | | | | | |
|---------------|-----------|---------------------------------|----|----|----|----|-----|------|-----|-------|-------|
| | | Fe | Ni | Cr | P | B | Si | C | Mn | Ti | Al |
| Metglas 2826A | Yes | 32 | 36 | 14 | 12 | 6 | -- | -- | -- | -- | -- |
| Metglas 2826 | Yes | 40 | 40 | -- | 14 | 6 | -- | -- | -- | -- | -- |
| T304 Steel | No | 69 | 8 | 20 | -- | -- | 1.2 | 0.00 | 1.7 | -- | -- |
| Incoloy 800 | No | 46 | 31 | 22 | -- | -- | -- | 0.00 | -- | 0.005 | 0.008 |

(a) Compositions are nominal, except that for T304 steel, which is a mill analysis.

solution. This approach is being used because it provides valuable information concerning corrosion kinetics to be expected within pits and crevices, in a relatively rapid manner and over a wide potential range. Thus, it is a convenient method for screening the corrosion behavior of the various alloys for subsequent in-depth evaluation in a simulated crevice geometry.

The experimental technique being used for this alloy screening is potentiodynamic polarization (PP). PP provides important information on corrosion kinetics as a function of oxidizing tendency, i.e., electrode potential. A single potential sweep can provide data on corrosion potential, severity of active dissolution, ease and degree of passivation, tendency for pitting, and transpassive dissolution.

Figure 1 illustrates a combined cathodic-anodic potential sweep in 1N NaCl, pH 2.4, for T304 steel. The critical pitting potential⁽²⁾, E_{cp} , for these experimental conditions is about -0.1 V(SCE), as evidenced by the increase in anodic current density and subsequent detection of pitting on the electrode surface by optical microscopy. Although a positive hysteresis (defined as a positive deviation in anodic current density by the return sweep relative to the forward, or anodic, sweep) occurred initially, it did not last until the original open circuit potential was reached. This behavior is not customary on pitted electrodes, since a positive hysteresis usually prevails throughout the return sweep. This behavior has been observed frequently during the pitting of amorphous and T304 foils, and at present we have no satisfactory explanation for it.

The polarization curve in Figure 1 should be contrasted with that in Figure 2, which indicates polarization behavior of BCL's Alloy 5 (14 atomic percent Cr). This alloy was polarized to 1.60 V(SCE), yet subsequent SEM examination indicated complete absence of pitting. This extreme resistance to localized corrosion attack is characteristic of amorphous Fe-Ni-Cr type alloys, and in fact is one of the most promising features for future exploitation in connection with these alloys. The first anodic peak, occurring at -0.30 V(SCE), represents active dissolution.

(2) E_{cp} is strongly dependent on sweep rate, surface preparation, and other experimental procedures.

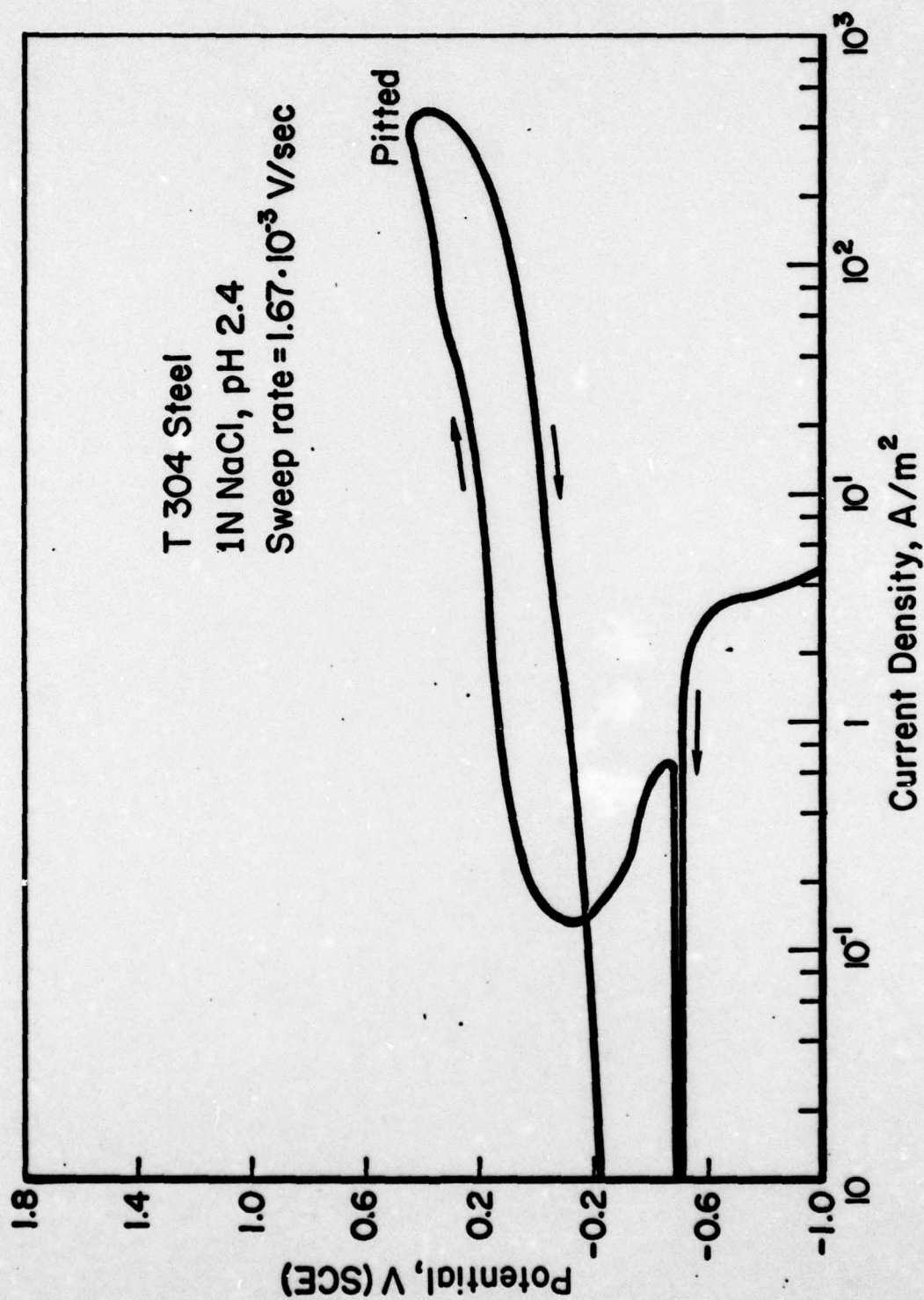


FIGURE 1. POTENTIODYNAMIC POLARIZATION CURVES FOR T304 STAINLESS STEEL IN A SIMULATED CREVICE ELECTROLYTE

This alloy began pitting at about -0.1 V(SCE) and was performed at the termination of the experiment.

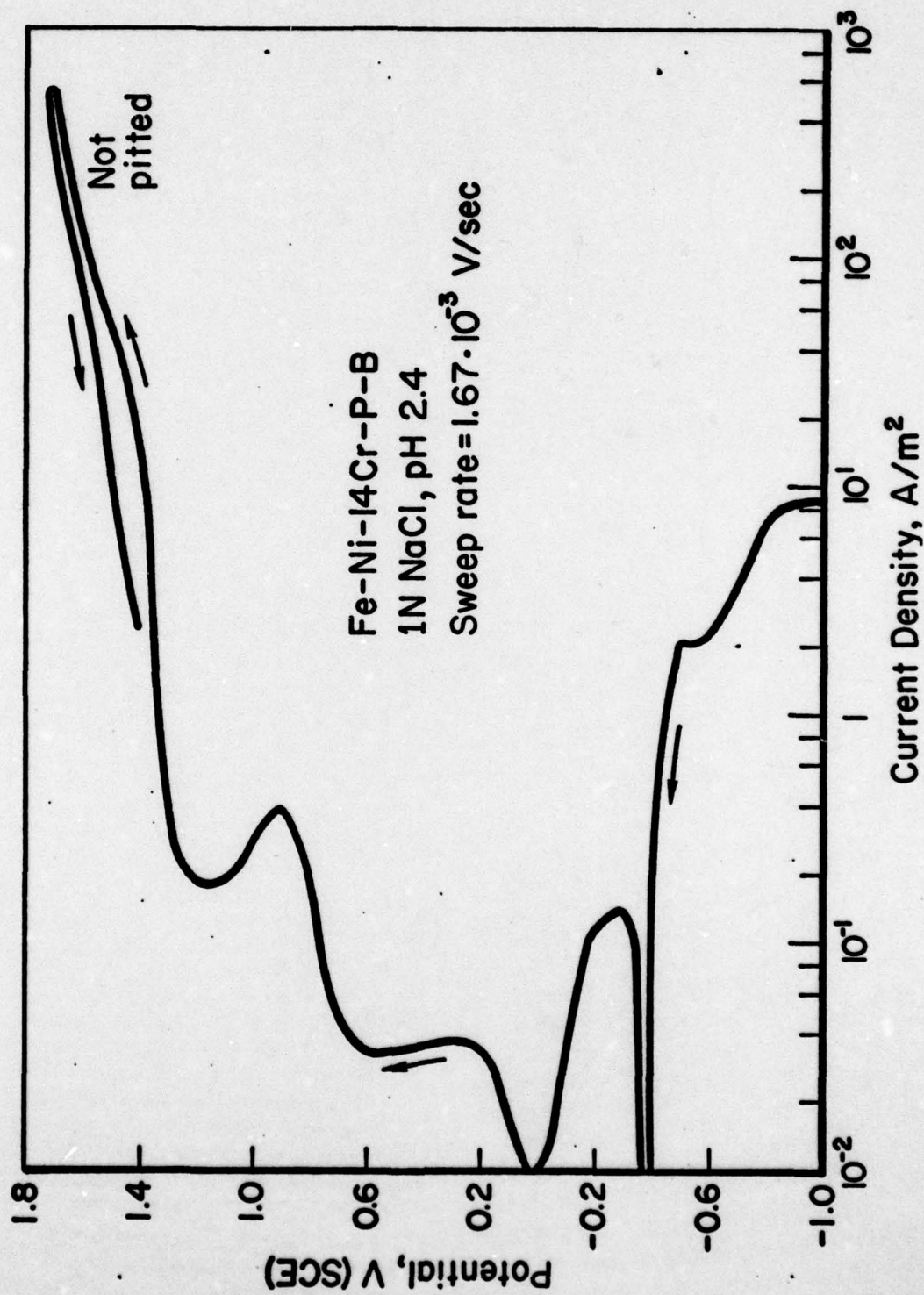


FIGURE 2. POTENTIODYNAMIC POLARIZATION CURVES FOR ALLOY 5 (14 ATOMIC PERCENT Cr) IN A SIMULATED CREVICE ELECTROLYTE

This alloy was not pitted at the termination of the experiment.

The current density at this peak, 0.14 A/m^2 , is the critical current density for passivation, i_c . The minimum current density in the passive region, i_p^{min} , was 0.095 A/m^2 and represents an extremely low value for such an aggressive electrolyte. The second anodic peak represents transpassivity, in this case the selective dissolution of chromium as the hexavalent ion, Cr^{+6} . The sharp increase of current beginning at about 1.25 V/(SCE) is due to oxygen evolution.

Polarization data were obtained from all of the alloys used in this program in the manner shown in Figures 1 and 2. The most important features of these polarization curves are i_c , because it indicates the ease of passivating the alloy, and i_p^{min} , because it is a measure of the degree of passivity attained. The variation of these quantities with chromium content of the alloy is shown in Figure 3. Several features are worth emphasizing with respect to the curves in this Figure:

- (1) Both i_c and i_p^{min} decrease with increasing Cr content of the alloy.
- (2) For the BCL alloys, i_c decreases by a factor of 30 as Cr is increased to 14 at. percent, which is a significant variation.
- (3) i_p^{min} decreases by a factor of only about 5; this is surprising, since the effect of Cr on passivation in such an aggressive electrolyte was expected to be greater.
- (4) i_p^{min} is only 0.05 A/m^2 for alloy 1, which contains no Cr. This is an extremely good degree of passivation for a non-Cr containing Fe-Ni alloy in an acid chloride solution.
- (5) Allied's Metglas 2826 (0 atomic percent Cr) is similar to Battelle's Alloy 1. Metglas 2826A (14 atomic percent Cr) is more difficult to passivate than Battelle's Alloy 5 (14 atomic percent Cr), and i_p^{min} is a factor of four greater for Metglas relative to Alloy 5.

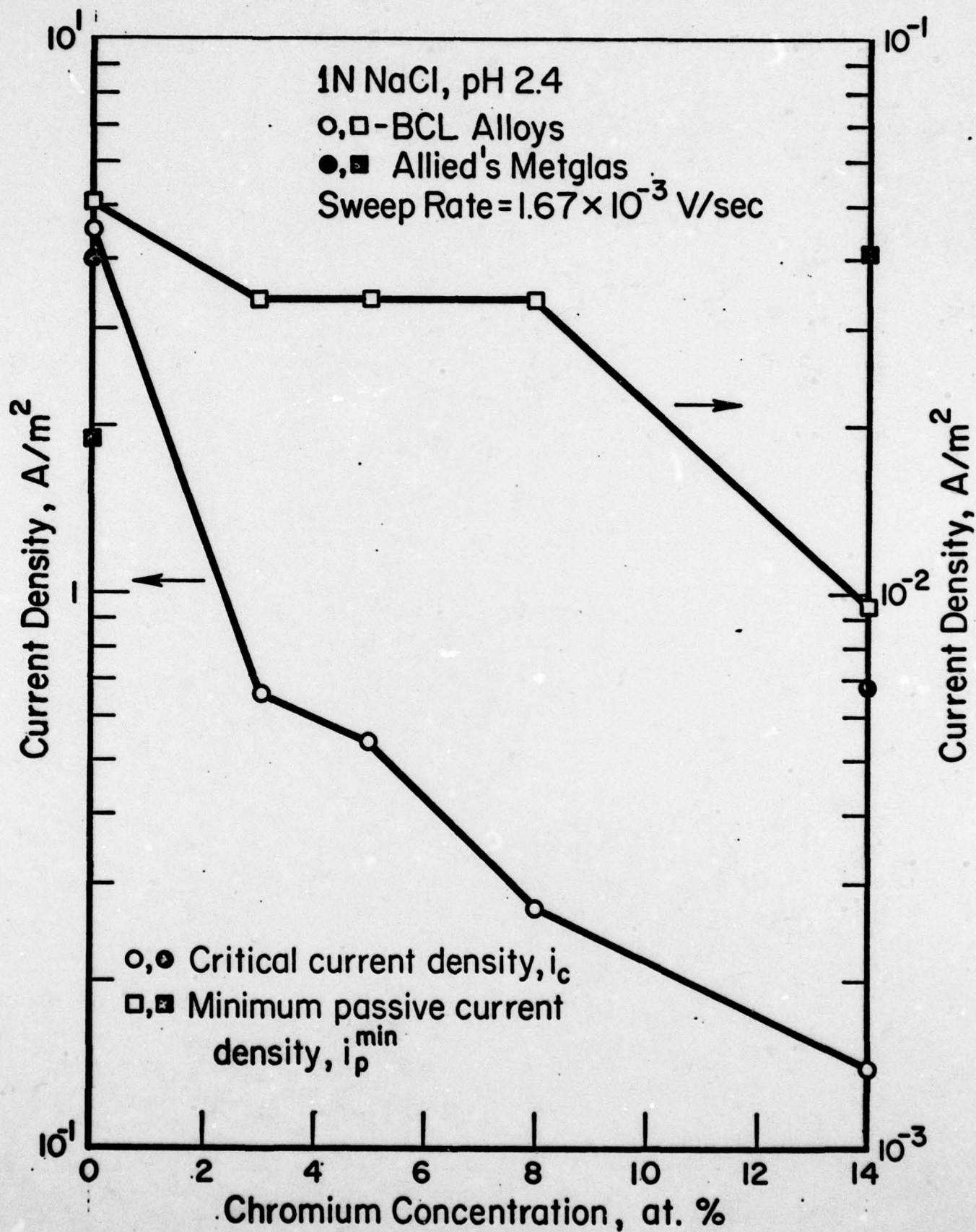


FIGURE 3. VARIATION OF i_c AND i_p^{min} WITH CHROMIUM CONCENTRATIONS FOR BCL AND METGLAS ALLOYS

The resistance of these alloys to localized corrosion was investigated in greater detail by potentiostatic polarization in acidified chloride electrolyte. Specifically, the electrode potential was increased to a predetermined value, held for a period of time, and then decreased to the open circuit potential. The current-time behavior was monitored continuously, and the electrodes were subsequently examined by SEM for evidence of pitting. Initiation and propagation of pitting corrosion was detected by this technique as a gradual increase of corrosion current with time, caused by loss of passivity at local regions and the onset of more rapid active dissolution.

Representative curves illustrating the use of this technique are shown in Figures 4 and 5. Figure 4 indicates that T304 stainless pits readily at 0.00 V(SCE), as verified by inspection of the corroded electrode surface. Figure 5 shows an extreme resistance to pitting by alloy 5 (14 atomic percent Cr); a 1 hour hold at 1.33 V(SCE) did not produce localized attack, again verified by careful microscopic examination.

Work Next Period

The preceding data were chosen to present only the highlights of results obtained to date. This preliminary screening of amorphous alloys in simulated crevice solutions indicates that crevice corrosion may not occur at significant rates, because of the ability of these alloys to form protective films in electrolytes which easily destroy films on conventional "corrosion resistant" materials. Future work will involve a transition to testing in a specially designed cell which simulates the restricted flow conditions characteristic of a crevice, and also measuring open circuit corrosion rates in sealed ampoules. Both techniques will cast more light on the role of dissolved oxygen in conferring this excellent passivity. This is important, because dissolved oxygen has been shown in previous unpublished research at Battelle to strongly influence corrosion behavior of amorphous alloys.

The crevice cell mentioned above has been designed and built, and the ampoule tests are underway.

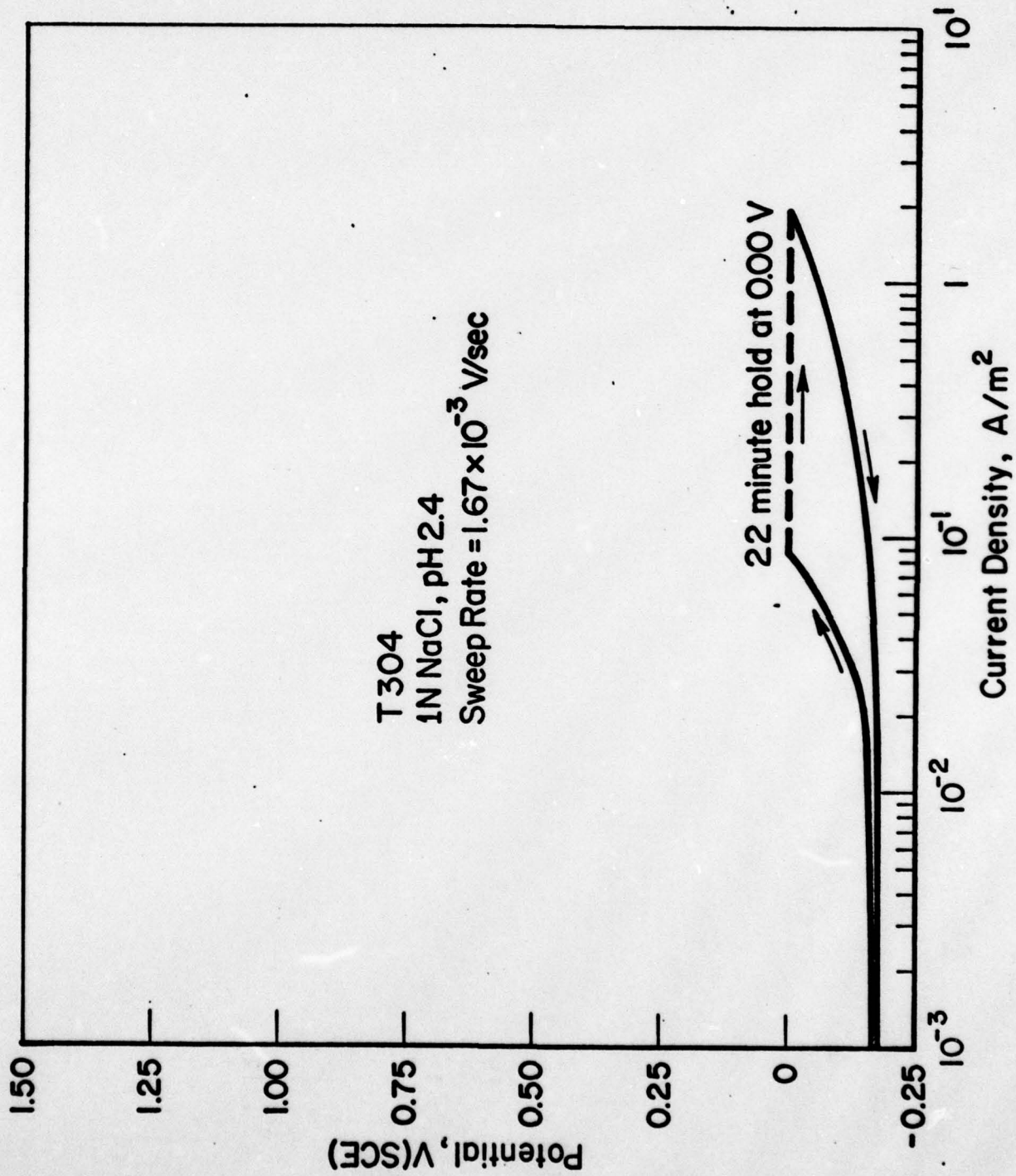


FIGURE 4. POTENTIOSTATIC CURRENT-TIME VARIATION FOR T304 STAINLESS STEEL

Electrode was pitted at termination of experiment.

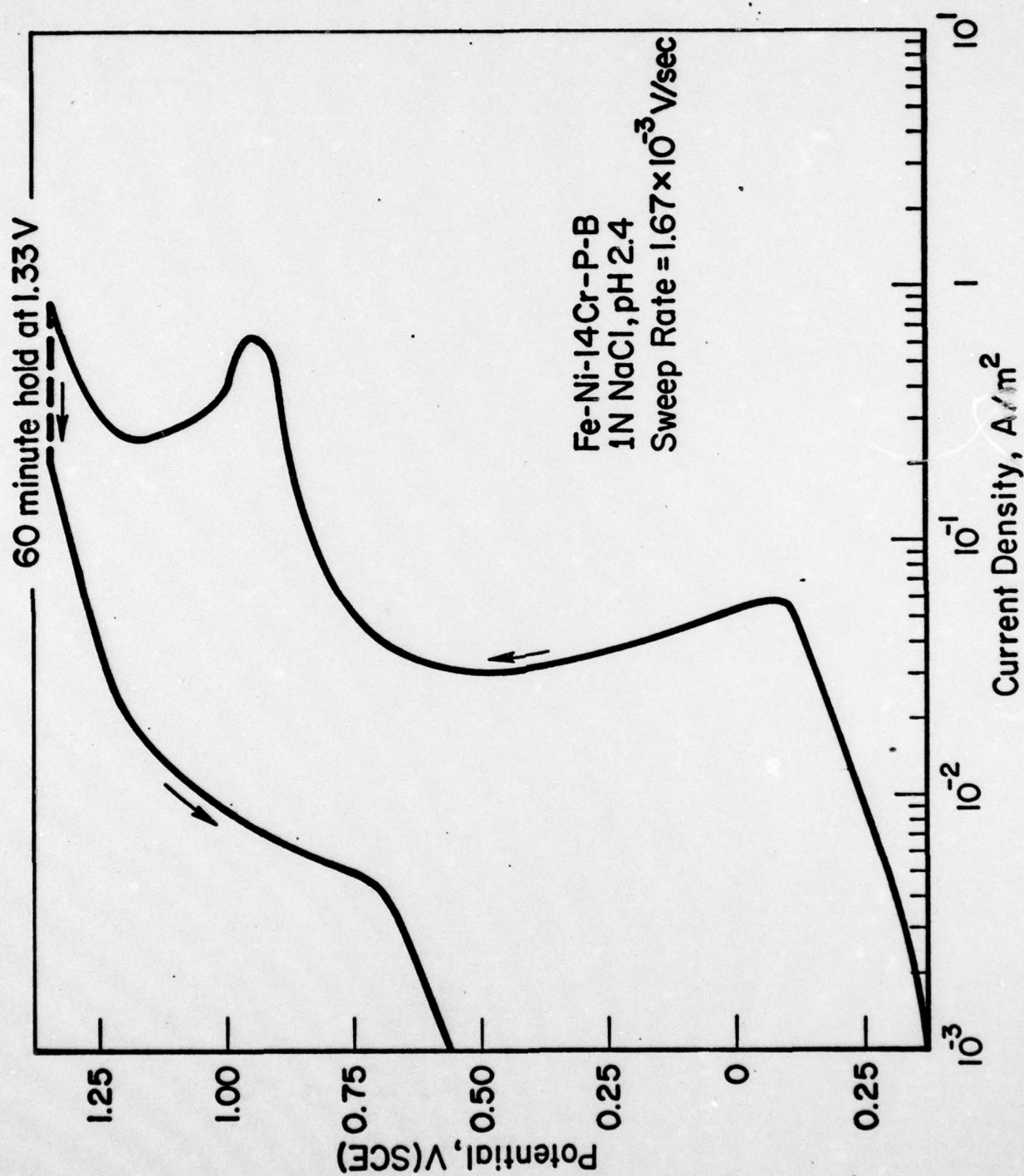


FIGURE 5. POTENTIOSTATIC CURRENT-TIME VARIATION FOR ALLOY 5 (14 ATOMIC PERCENT CR)

Electrode was not pitted after the experiment.

Phase 2. Developing a Sputtering Procedure
for Applying Amorphous Corrosion Resistant Alloys

Approach

Two sputtering techniques, r.f. diode or d.c. magnetron, will be used to deposit selected materials believed to have corrosion resistant properties in the amorphous form. Deposits for evaluation will be condensed onto a platinum foil substrate, bonded by a material such as indium to a liquid nitrogen-chilled substrate holder to ensure good thermal contact. The corrosion behavior of the deposits will be determined by using potentiodynamic polarization in acidified chloride solutions to measure the ease and degree of passivation exhibited by the deposits.

Alloy Preparation

Two alloys have been obtained for use as sputtering targets. One is conventional T304 stainless steel, the other, 36 Fe-30Ni-14Cr-14P-6B (atomic percent). The stainless steel is being used for the initial deposition experiments in an attempt to duplicate the work by Nowak,⁽³⁾ who successfully deposited a partially amorphous, corrosion resistant layer from a T304 steel target. The second composition listed above will be used for later work, after the optimum deposition techniques have been identified.

Work Accomplished This Period

Work this period has focused on modification of sputtering equipment to meet the specialized requirements of amorphous metal deposition. The basic approach to be tried initially involves sputtering at low rates (of the order of 10-100 $\mu\text{m}/\text{sec}$) onto a substrate chilled by liquid nitrogen. The low sputtering rates will minimize the need for

(3) Nowak, W. B., "Microcrystalline/Amorphous Iron Alloy Films for Corrosion-Resistant Coatings", Mat. Sci. Eng., 23 301 (1976).

heat dissipation, which will be readily accomplished through the cold substrate. Nowak has shown that such an approach can yield partially amorphous Fe-Ni-Cr-Si deposits with improved corrosion resistance relative to the crystalline state.

A specially designed stainless steel chamber, turbomolecularly pumped and capable of pressures of 10^{-7} torr, is being used. When used for the sputtering experiments, a high flow rate of argon gas will be employed to purge the chamber of any contaminants. A titanium getter operating at 700 C provides for the purification of 120 sccm of argon used to maintain the normal 5m torr sputtering pressure. The sputtering cathode which will be used will be either rf or d.c. magnetron. A substrate holder has been fabricated from copper, and it contains an internal cavity for liquid nitrogen. Insulated cryogenic feedthroughs have been purchased and are ready for installation.

Work Next Period

Work during the next 6 month period includes installation of the substrate holder, cryogenic feed system and thermocouple monitoring into the sputtering chamber. The stainless steel target will be mounted on the magnetron cathode for preliminary experiments. The deposits will be condensed on platinum foil substrates bonded to a nitrogen chilled surface to ensure good thermal contact and heat transfer. The deposits then will be characterized by a combination of techniques including potentiodynamic polarization (to determine corrosion resistance), transmission electron microscopy (to determine the state of crystallinity), and SEM (to characterize surface topography and nature of corrosive attack). It is emphasized that potentiodynamic polarization will be used to screen the deposits, and only the more promising will be studied in detail.

Summary

The aqueous corrosion phase of the program is currently on schedule. Results look promising for all five amorphous BCL alloys,

since they exhibit considerable resistance to corrosion in a simulated crevice solution, even at very oxidizing potentials. Work is somewhat ahead of schedule on the sputtering phase; experimental deposits suitable for evaluation will be available next period.